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Impact of photocatalyst optical properties on the efficiency of solar photocatalytic reactors rationalized by the concepts of initial rate of photon absorption (IRPA) dimensionless boundary layer of photon absorption and apparent optical thickness

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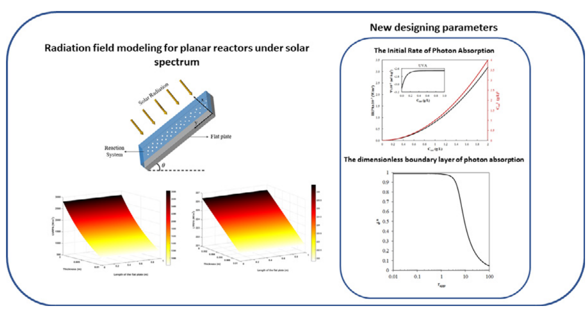
HIGHLIGHTS

- Initial rate of photon absorption (IRPA) correlated to optimum catalyst concentration.
- τ_{app} provides an ideal similarity parameter for designing and scaling photocatalytic reactors.
- τ_{app} in the range 4.1–4.4 provides optimum catalyst and reactor performance with any photocatalyst.
- Dimensionless boundary layer of photon absorption of 90% provides optimal design.
- Radiative transfer phenomena correlated to IRPA, dimensionless boundary layer of photon absorption and τ_{app}.

GRAPHICAL ABSTRACT



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ABSTRACT

The concepts of "initial rate of photon absorption" (IRPA), "dimensionless boundary layer of photon absorption" and "apparent optical thickness (τ_{app})" are presented to evaluate the radiative transfer phenomena in solar, slurry, planar, photocatalytic reactors. The radiation field produced by suspensions of TiO_2 and goethite, two photocatalysts with profoundly different optical properties used in heterogenous photocatalysis and heterogeneous photo-assisted Fenton reactions, was determined by the six-flux radiation absorption-scattering model coupled to the Henyey-Greenstein scattering phase function (SFM-HG). The concept of IRPA, defined by the differentiation at the local volumetric rate of photon absorption (LVRPA) at the reactor window boundary, is proposed as a new approach to determine the impact of catalyst loading and optical properties on the extinction of light inside a photoreactor. The IRPA showed that the extinction of light follows a second order dependency on the photocatalyst concentration while the impact of the optical properties can be expressed by a decoupled function (Ψ function). The Ψ function increased with photocatalyst concentration and approached a maximum at the same optimal photocatalyst concentration determined from the analysis of the total rate of photon absorption (TRPA) in the reactor. The analysis of TRPA and boundary layer of photon absorption redefined here in dimensionless form, as a function of τ_{app}, determined that the most efficient rate of radiation absorption in solar powered planar reactors occurs at τ_{app} = 4.1–4.4, with approximately 10% of the reactor width under darkness.

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τ_{app} is a similarity dimensionless parameter exclusively derived from the SFM approach, which clusters the effects of photocatalyst loading, reactor dimension and photocatalyst optical properties, providing an ideal parameter for designing and scaling photocatalytic reactors operated with any kind of photocatalytic material.

1. Introduction

Platform technologies such as heterogeneous photocatalysis and the photo-assisted heterogeneous Fenton process have shown great potential for the treatment of contaminated water or air [1,2]. The main attraction of these processes is the utilization of solar light as the driving force for the production of highly oxidative radical species, which are then able to complete the conversion of water or air contaminants to innocuous products.

One very active field of research in heterogeneous photocatalysis is the development and evaluation of new photocatalytic materials. Doping of commercial titanium dioxide (TiO_2) is a common approach to extend the absorption spectrum of TiO_2 from the UV into the visible region of the solar spectrum [3]. Furthermore, iron oxides, have shown interesting properties as visible light active photocatalyst, as well as, catalysts for photo-assisted heterogeneous Fenton reactions when combined with hydrogen peroxide [4–6].

The intense development in new photocatalysts calls for the development of comprehensive methodologies for the analysis of the radiative transfer behavior of these new materials, particularly in the solar radiation spectrum. These methodologies are necessary for an appraisal of the catalytic performance of new photocatalytic materials and for the design and optimization of solar photoreactors. For this purpose, the optical properties of existing or new photocatalysts (the extinction, absorption and scattering coefficients and the scattering phase function) must be determined or estimated.

Recently several authors have investigated the influence of the optical properties on the photocatalyst performance [7–9], however, the literature has scarce information on the application of these for reactor design. Besides, available information deals almost exclusively with TiO_2 P25 photocatalyst. Furthermore, optimized photoreactor designs have been proposed in conjunction with TiO_2 photocatalytic powders, however, it remain unclear if these designs are also optimal when the reactor is loaded with other photocatalysts, particularly those materials having highly different optical properties than TiO_2. Process intensification, for instance, is a novel and very interesting approach for optimizing photocatalytical processes [10,11]. One aspect that the intensification process should consider firstly is the optical performance of the photocatalytical material (i.e. its optical properties) for an integral design or correct selection of the photoreactor. In general, the optimization of the reactor performance requires a detailed analysis between the operational parameters such as, optimal photocatalyst loading, which in turn depend on the optical properties of the synthesized material and the rate of absorption of radiation.

In this study, an alternative reaction engineering approach including the impact of the photocatalyst optical properties on the optimization of photoreactors is presented i.e. in the determination of an optimal catalyst loading or photoreactor size. The concepts of “initial rate of photon absorption” (IRPA) and “boundary layer of photon absorption” [12] redefined in dimensionless form are here proposed as new parameters for evaluating the impact of photocatalyst loading on the total rate of photon radiation absorption (TRPA) and to facilitate the optimal design of photoreactors at different scales, from laboratory scale to full scale. The consequence of these are far reaching since the evaluation of the wide range of photocatalysts reported in literature may have to be reconsidered, if the photocatalysts activity was determined at equal loadings in the reactor without accounting the impact of the photocatalysts optical properties.

Goethite (α-FeOOH), an iron oxide used as visible-active photocatalysts [13] as well as for photo-assisted heterogeneous Fenton reactions [14,15], and the extensively explored TiO_2 P25 were selected to illustrate the impact of the above methodology on materials with significantly different optical properties. The use of goethite as one of the model photocatalysts also offers an illustration of the evaluation of the radiative transfer phenomena of a photocatalyst active in the visible range of the solar spectrum, which may be the of special interest to the literature. The optical performance of these photocatalysts was evaluated in a simple planar photoreactor geometry, allowing the results and concepts of this study to be easily transferred to other photoreactor geometries. Such geometry is characteristic of falling liquid films [16] and conventional flat-plate photoreactors, with the slurry photocatalyst suspension confined between two walls [17,18]. The six-flux absorption scattering model (SFM) was used to model the solar radiation transport through slurry suspensions of the photocatalysts.

2. Mathematical methods

2.1. Optical properties of photocatalysts and solar spectral irradiation

The spectral absorption and scattering coefficients of the photocatalysts TiO_2 (P25, Evonik) and goethite (α-FeOOH, Aldrich) in aqueous suspensions [19,20] are shown in Fig. 1 and Fig. 2, including the solar radiation data of global irradiance (AM 1.5), incident on a plane tilted 37° facing the sun [21]. The wavelength range of 310–500 nm was selected since 300 nm is the lower wavelength in which both the goethite and TiO_2 interact with light and 500 nm is the upper limit for goethite, beyond this value Ortiz de la Plata et al. [20] found that the absorption of radiation by goethite was too small to be taken into account. Similarly, the graphical representation of the Henyey-Greenstein scattering factor is presented in Fig. S1 (Supporting Information (SI)).

2.2. The six flux model for radiation field calculations

The spatial distribution of the local volumetric rate of photon absorption (LVRPA) inside the planar reactor was evaluated by the SFM as shown in Eq. (1) [22]:

$$e^a(x) = \frac{I_0\tau_{app}}{\omega_{corr}(1-\gamma)L}[(\omega_{corr}-1+\sqrt{1-\omega_{corr}^2})e^{-x\tau_{app}/L} + \gamma(\omega_{corr}-1-\sqrt{1-\omega_{corr}^2})e^{x\tau_{app}/L}] \quad (1)$$

where a, b, ω_{corr} and γ are SFM parameters defined as follows:

$$a = 1-\omega p_f-\frac{4\omega^2 p_s^2}{1-\omega p_f-\omega p_b-2\omega p_s} \quad (2)$$

$$b = \omega p_b+\frac{4\omega^2 p_s^2}{1-\omega p_f-\omega p_b-2\omega p_s} \quad (3)$$

$$\omega_{corr} = \frac{b}{a} \quad (4)$$

$$\gamma = \frac{1-\sqrt{1-\omega_{corr}^2}}{1+\sqrt{1-\omega_{corr}^2}}e^{-2\tau_{app}} \quad (5)$$

the apparent optical thickness τ_{app} is:

$$\tau_{app} = a\tau\sqrt{1-\omega_{corr}^2} \quad (6)$$

For a planar geometry, the optical thickness τ is defined by:

$$\tau = (\sigma^*+\kappa^*)C_{cat}L \quad (7)$$